USSR/Physical Chemistry - Solutions. Theory of Acids and Bases, B-11

Abst Journal: Referat Zhur - Khimiya, No 1, 1957, 489

Abstract: activity of the acid determined from the emf or from the vapor pressure and c_{A-} is the concentration of the halide ion.

Card 2/2

0017

THE ACIDITY FUNCTIONS OF BORIC AND
PHOSPHORIC ACID SOLUTIONS. L. Vinnik, P. N.
Kreshov, and N. M. Colubeva (Inst. of Physical Chemistry,
Acad. of Sciences USSR) Zhur. Fiz. Khim. 31, 653-5

(1957) (in Russian).

The acidity functions of boric fluoric acid and its
phosphoric acid have been measured by the indicator

AUTHOR:
TITLE:

PERIODICAL:

ABSTRACT:

20-6-37/59

ENTELIS, S.G., and CHIRKOV, N.M.
The Thermodynamics of Propylene Hydrochlorination.
(Termodinamika reaktsii gidrokhlorirovaniya propilena. Russian).
Doklady Akademii Nauk SSSR, 1957, Vol 113, Nr 6, pp 1318 - 1320
(U.S.S.R.)

The hydrochlorination reaction of __ .

20-6-37/59

The Thermodynamics of Propylene Hydrochlorination,

tained coincides well with the value calculated by means of the tables.
From table 3 we see mainly that reversibleness begins only at 120°. At
100° and all the more at 70° reversibelness is low. (2 illustrations,
3 tables).

ASSOCIATION: Institute for Chemical Physics of the Academy of Science of the USSR.
               (Institut Khimicheskoy fiziki Akademii nauk SSSR).
PRESENTED BY: V.N. KONDRAT'YEV, Member of the Academy
SUBMITTED: 6 November 1956
AVAILABLE: Library of Congress

Card 2/2

AUTHORS: Entelis, S. G., Petrakovich, V. Ye., Korovina,G.V.,   20-114-4-46/63
             Chirkov, N. M.

TITLE: The Kinetics of the Formation of Alcohol and Alkyl Acid in the
             Reaction of Propylene With a Water Solution of Sulphuric Acid.
(Kinetika obrazovaniya spirta i alkilkisloty pri reaktsii propilena s vodnoy sernoy kislotoy)

PERIODICAL: Doklady Akademii Nauk SSSR, 1957, Vol. 114, Nr 4, pp. 848-851
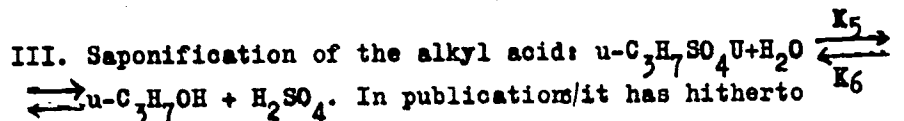   (USSR)

ABSTRACT: A number of papers was devoted to the investigation of the
             absorption kinetics of olefines by sulphuric acid. The majority
             of the works, that of Rustamov excepted, have a common funda-
             mental deficiency: they were performed under conditions in which
             the absorption velocity is limited by diffusionprocesses. The
             authors studied the absorption kinetics of propylene by 67%-
             -sulphuric acid at 42-90°C and an initial pressure of ~800 torr.
             The complicated acid-catalytic processes of propylene in sul-
             phuric acid may be described roughly for the dissolution as
             three reversible reactions:

     I. Formation of alkyl acid: $C_3H_6 \underset{K_2}{\overset{K_1}{\rightleftarrows}} u\text{-}C_3H_7SO_4H.$

     II. Direct Formation of alcohol: $u\text{-}C_3H_6 + H_2O \underset{K_4}{\overset{K_3}{\rightleftarrows}} u\text{-}C_3H_7OH.$

Card 1/3

The Kinetics of the Formation of ^{A}lcohol and Alkyl Acid in the   2o-114-4-46/63
Reaction of Propylene With a Water Solution of ^{S}ulphuric Acid.

III. Saponification of the alkyl acid: $u-C_3H_7SO_4U+H_2O \underset{K_6}{\overset{K_5}{\rightleftharpoons}}$

$\rightleftharpoons u-C_3H_7OH + H_2SO_4$. In publications/it has hitherto
not been recorded whether the chief amount of alcohol is ob-
tained by II. or III. However, the fact of a parallel accumu-
lation of alcohol itself excludes reaction III. The experimen-
tal curves obtained are compared with the theoretical ones.
Two cases were assumed: 1. no saponification of the alkyl acid
occurs, 2. alcohol forms parallel to $u-C_3H_7SO_4H$ as well as by
saponification of the latter. From the described short analysis
it may be concluded that the chief, if not the total,,amount of
alcohol does not result from saponification of $u-C_3H_7SO_4H$, but
develops: parallel with it during the C_3H_6 reaction in water.
There are 4 figures, 2 tables, and 8 references, 5 of which are
Slavic.

ASSOCIATION: Institute for Chemical Physics of the AS USSR (Institut
khimicheskoy fiziki Akademii nauk SSSR)

PRESENTED: January 19, 1957 by V. N. Kondrat'yev, Member, Academy of
Card 2/3

The Kinetics of the Formation of Alcohol and Alkyl Acid in the
Reaction of Propylene With a Water Solution of Sulphuric Acid   20-114-4-46/63

Sciences, USSR

SUBMITTED: January 16, 1957

Card 3/3

AUTHORS: *CHIRKOV, N.M.*
Vinnik, M. I. , Ryabova, R. S. , Chirkov, N. M.   20-6-27/47.

TITLE: The Kinetics of the Acid-Catalytic Decarbonylation of Benzoyl Form-
ic Acid (Kinetika kislotno-kataliticheskogo dekarbonilirovaniya
benzoilmurav'inoy kisloty)

ABSTRACT: The present paper investigates the determination of particles par-
ticipating in the elementary act of the acid processes and com-
pares the constant of speed with the concentration of the particles.
The reactions $C_6H_5COCOOH \rightarrow CO + C_6H_5COOH$ were selected as model.
The solutions of benzoyl formic acid in water and in diluted solu-
tions of sulphuric acid do not absorb in the visible range of the
spectrum. On dissolution of $C_6H_5COCOOH$ in concentrated H_2SO_4 (80 -
- 90 %) an absorption in the visible range of the spectrum appears.
The absorption coefficient of benzoyl formic acid considerably in-
creases with increasing concentration of H_2SO_4. In the present
work the speed of the decarbonylation of solutions of $C_6H_5COCOOH$ in
H_2SO_4 was determined from the speed of the decrease in the optical
density of the solution when $\lambda = 400$ mμ. The optical density
was measured by the spectrometer (ϕ - 4) in quartz cuvettes. A
diagram illustrates a typical kinetic curve of the decarbonylation

Card 1/3

The Kinetics of the Acid-Catalytic Decarbonylation of Benzoyl Formic Acid

20-6-27/47

process (the dependence of the optical density D of the solution on the time t) and its logarithmic anamorphosis. The influence of the acidity h_0 upon the constant K of the speed was investigated in the range of concentrations of from 85,46 to 99,94 % of H_2SO_4 at T = 15°C. The corresponding results are illustrated by a diagram. In the range from h_0 = $10^{8,06}$ to h_0 = $10^{9,4}$ the dependence between lg K and the acidity function H_0 is linear: lg K + 1,8 H_0 = const. At higher values of acidity a deviation from the linearity was observed. The temperature dependence of K for the solutions of $C_6H_5COCOOH$ in 98,80; 96,2; 92;89,77 and 85,46 % H_2SO_4 were determined in a narrow range of temperature. These data are in agreement with the Arrhenius (Arrenius) equation. Benzoyl formic acid is supposed to exist in different forms in the concentrated and diluted solutions of H_2SO_4. In diluted H_2SO_4 it is supposed to exist in a nonionized state, but with increasing acidity of the medium it is ionized. Then the authors report on the determination of the constant of alkalinity. There are 4 figures, 1 table, and 1 non-Slavic reference.

Card 2/3

The Kinetics of the Acid-Catalytic Decarbonylation of Benzoyl Formic Acid   20-6-27/47

ASSOCIATION: Institute of Chemical Physics AS USSR
              (Institut khimicheskoy fiziki Akademii nauk SSSR)

PRESENTED: June 17, 1957, by V. N. Kondrat'yev, Academician

SUBMITTED: June 12, 1957

AVAILABLE: Library of Congress

Card 3/3

CHIRKOV, N.M., Doc Chem Sci—(diss) "On an acid heterogenous

catalysis." Mos, 1958. 16 pp (Acad Sci USSR. Inst of Chem Physics),

110 copies. Bibliography at end of text (15 titles) (KL, 22-58,102)

— 14 —

20-119-1-26/52

AUTHORS: Vinnik, M. I., Manelis, G. B., Epple, G. V., Chirkov, N. M.

TITLE: Kinetics of Isobutylene Polymerization in the Presence of Boron Fluoride Etherate (Kinetika polimerizatsii izobutilena v prisutstvii efirata ftoristogo bora)

PERIODICAL: Doklady Akademii Nauk SSSR,1958,Vol.119,Nr 1,pp.98-100(USSR)

ABSTRACT: The present paper investigates the polymerization of iC_4H_8 in the presence of a complex compound of the diethyl ether with boron fluoride: $(C_2H_5)_2O \cdot BF_3$. The catalyst $(C_2H_5)_2O \cdot BF_3$ in the form of a thin adsorbed film was applied to the surface of little tubes of melted quartz for the purpose of avoiding diffusion-conditioned disturbances. The reaction container with an insertion of little quartz tubes was evacuated to a pressure of from 10^{-4} - 10^{-5} mm of mercury column previous to the experiment. At first the necessary pressure of ether vapor was produced in the reaction container and then the boron fluoride was introduced. In every experiment the pressures of etherate $(P^g_{etherate})$ of boron fluoride $(P^g_{BF_3})$, of ether in the gaseous phase (P^g_{ether}), corresponding

Card 1/3

20-119-1-26/52

Kinetics of Isobutylene Polymerization in the Presence of Boron Fluoride
Etherate

to the equilibrium and the quantity of the etherate($P^{fl}_{etherate}$)
condensed on the surface were determined. The data used for
the determination of these values are given in brief. Special
attention was paid to the production of the pure reagents
which must not contain any traces of moisture. The reaction
velocity was expressed by the reduction of the isobutylene
pressure referring to 1 mole of the adsorbed etherate. A dia-
gram shows the kinetic curve and its anamorphosis for the
polymerization process of iC_4H_8 in the presence of the
etherate $(C_2H_5)_2O \cdot BF_3$. If $t = 70°C$ and $P_{iC_4H_8}$ is small

(up to 100 - 1500 mm of mercury column), the kinetic equation
up to a 40 - 50 per cent transformation can easily be ex-
pressed by a secondary order equation. The constant of velo-
city K_4 thus determined does not depend on the initial pres-
sure of the iC_4H_8. The influence of ether on the catalytic
activity of the $(C_2H_5)_2O \cdot BF_3$ is similar to the influence of
water on the acidity of mineral acids (phosphoric acid, sul-
furic acid etc.). Such an intense influence of the ether -
even at low concentrations - can only be explained by its

Card 2/3

20-119-1-26/52

Kinetics of Isobutylene Polymerization in the Presence of Boron Fluoride Etherate

basic properties. A diagram and a table illustrate the dependence of the constant K_1 of the polymerization velocity on the pressure of boron fluoride in gaseous phase corresponding to the equilibrium. The etherate of boron fluoride is an effective catalyst for the polymerization of iC_4H_8. Judging from the catalytic activity the etherate must have the properties of an intense acid. There are 3 figures, 1 table, and 7 references, 3 of which are Soviet.

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR
(Institute for Chemical Physics AS USSR)

PRESENTED: August 7, 1957, by V. N. Kondrat'yev, Member, Academy of Sciences, USSR

SUBMITTED: August 1, 1957

Card 3/3

AUTHORS: Chirkov, N, M,, Rustamov, Kh. R.   76-32-2-2/38

TITLE: The Alkylation of Benzene With Olefines (Alkilirovaniye
               benzola olefinami)
               IV. On the Reaction Process (IV. O mekhanizme reaktsii)

PERIODICAL: Zhurnal Fizicheskoy Khimii, 1958, Vol. 32, Nr 2, pp. 219-223
               (USSR)

ABSTRACT: Based on the experimental data obtained the authors give the
               probable reaction process of the alkylation of benzene with
               olefines. The first stage of the process is the absorption
               of the reagents by the acid. In the absorption of propylene
               by sulfuric acid (and by protonic acids at that) propylene
               can exist in the following states: C_3H_6 (in physically
               dissolved state), $C_3H_7^+$ (as a carbon ion), $C_3H_7HSO_4$ and
               $(C_3H_7)_2SO_4$. The possibility of their presence was stated by
               the authors in the investigation of the absorption of
               olefines by sulfuric acid and phosphoric acid (ref. 7). The
               authors show that in the alkylation of benzene with olefines,
Card 1/4   e. g. propylene, in the presence of sulfuric acid the

The Alkylation of Benzene With Olefines.
IV. On the Reaction Process   76-32-2-2/38

following particles can be present in the solution: C_3H_6, $C_3H_7^+$, $C_3H_7HSO_4$, $(C_3H_7)_2SO_4$, C_6H_6, $C_6H_7^+$. In the inter- action of these particles the following two forms can develop: Isopropylbenzene and di-isopropylbenzene. As regards the catalyst it can, in principle, take part here in two forms: in ion form or in the form of non-dissociated molecules. When the concentration of sulfuric acid is increased by 10% its thermodynamic activity increases 2,6 fold and the velocity of reaction increases 80 fold. Such a great change of velocity can only be explained by starting from the ion conceptions. The several possible variants of the process are given and the authors show that the scheme: $C_6H_7^+ + C_3H_7HSO_4$;

$C_6H_7^+ + (C_3H_7)_2SO_4$ best explains all experimental results ob- served as well as in particular the influence of the acid concentration on the velocity constant of alkylation. According to this scheme the dependence of the velocity constant on the function of the acid somewhat exceeds the first power, which coincides with experimental data.- It is assumed that the reaction process in principle is of ion character. The most probable processes in the formation of

Card 2/4

The Alkylation of Benzene With Olefines. 76-32-2-2/38
IV. On the Reaction Process

mono- and dipropylbenzene are put down and it is shown that
for the formation of monoalkylbenzenes the reaction
$C_6H_7^+ + C_3H_7HSO_4 \rightarrow C_3H_7C_6H_5 + H_3SO_4^+$ represents the limiting
stage, while for the formation of dialkylbenzene the reaction
$C_6H_7^+ + (C_3H_7)_2SO_4 \rightarrow (C_3H_7)_2C_6H_4 + H_3SO_4^+$ represents this
stage. The correctness of the suggested process of reaction
could be checked by the computation of the reaction velocity
from the number of collisions. For this the real activation
energy of the reaction as well as the concentration of the
reacting component must be known. The actual activation
energy for the reaction of the alkylation of benzene with
propylene in the presence of sulfuric acid is, according to
the scheme given, equal to 21,4 kcal/Mol. As regards the
computation of the concentration of reagents the ether con-
centration can be computed from the data on the absorption
of olefines by acids (ref. 7). The computations of the
concentration of the carbon ion of benzene starting from the
velocity, showed 10^{-5} Mol/ml which does not contradict to
the suggested process of reaction. There are 9 references,

Card 3/4

The Alkylation of Benzene With Olefines.   76-32-2-2/38
IV. On the Reaction Process

            5 of which are Soviet.

ASSOCIATION: Akademiya nauk SSSR, Institut khimicheskoy fiziki, Moskva
                (Institute for Chemical Physics, AS USSR, Moscow)

SUBMITTED: March 7, 1956

            1. Benzenes--Synthesis   2. Ethylenes--Chemical reactions
            3. Ethylenes--Absorption   4. Propenes--Absorption

Card 4/4

SOV/76-32-9-36/46

AUTHORS: Entelis, S. G., Tsikulin, M. A., Volkov, L. V., Chirkov, N. M.

TITLE: Methods and Apparatus of Physical-Chemical Research (Metody i tekhnika fiziko-khimicheskogo issledovaniya) The Determination of the Specific Surface Areas of Porous Bodies and Powders by the Method of Gaseous Flow (Izmereniye udel'noy poverkhnosti poristikh tel i poroshkov metodom istecheniya razrezhennogo gaza)

PERIODICAL: Zhurnal fizicheskoy khimii, 1958, Vol 32, Nr 9, pp 2187-2191 (USSR)

ABSTRACT: The specific surface area of porous bodies can be measured using a gaseous flow in the Knudsen pressure range, which is described in the papers of B. V. Deryagin and his co-workers (Refs 1 and 2). The present paper describes an improved and simpler apparatus (Figs 4 and 5). The formula given by Deryagin was used in conversions in carrying out determinations. Using this method the specific surface areas of the following substances were determined (Tables 1 and 2): porous glass (Shott Nr 4, Iena); porous glass (Shott Nr 3, Druzhnaya Gorka); porous porcelain (svecha Chemberlena); birch charcoal; aluminum

Card 1/2

SOV/76-32-9-36/46

Methods and Apparatus of Physical-Chemical Research. The Determination of the Specific Surface Areas of Porous Bodies and Powders by the Method of Gaseous Flow

silicate; untreated kaolin as well as kaolin which had been heated previously to 800°; porous quartz; burned chamotte; NB powder; tetranitro penterythrite; hexagene; and trinitrotoluene (TNT). There are 5 figures, 2 tables, and 4 references, 3 of which are Soviet.

ASSOCIATION: Akademiya nauk SSSR, Institut khimicheskoy fiziki, Moskva (AS USSR, Moscow Institute of Chemical Physics)

SUBMITTED: December 27, 1957

Card 2/2

5(4).

SOV/20-121-6-24/45

AUTHORS: Korovina, G. V., Entelis, S. G., Chirkov, N. M.

TITLE: The Velocity of the Absorption of Ethylene and Propylene by Sulfuric Acid of Various Concentrations (Skorost' poglo-shcheniya etilena i propilena sernoy kislotoy raznykh kontsentratsiy)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol 121, Nr 6, pp 1038-1040 (USSR)

ABSTRACT: In the first part of this paper, the authors discuss some previous papers dealing with this subject. The real kinetics of the absorption of propylene and ethylene by sulfuric acid were investigated at $70°$ by means of a circulation apparatus which was described in one of the authors' previous papers (Ref 3). In the course of the experiment, gas pressure remained constantly equal to atmospheric pressure. The velocity of the absorption was measured by determining the decrease of the gas quantity in the gas burette. If only the initial kinetic curve of the absorption (with respect to the gross weight) is taken into consideration (in disregard of reversibility), the equation $d\Delta v/dt = k'P$ may be used for the

Card 1/3

The. Velocity of the Absorption of Ethylene and Propylene by Sulfuric Acid
of Various Concentrations

calculations. Δv denotes the variation of the volume of the
gaseous phase reduced to standard conditions, and P - the
pressure of the gas in the system. For k', the equation

$k' = 22,4.10^3 \ kqv_k$ is given. A table contains the data of the

experiments concerning the absorption of propylene and ethylene
by sulfuric acid of various concentrations. According to these
results, there is a linear relation between the logarithm
of the constant of the absorption velocity of the olefine
and the function of the acidity of the medium:
$\lg k = -1,1 \ H_0 - 7,77$ for ethylene and $\lg k = -0,97 \ H_0 - 3,24$

for propylene. In the process of alcohol formation and al-
kylation (which are the elements of the absorption of the
olefines by the acid) the limiting stage is preceded by the
same process of olefine protonization. The proportionality
between the observed constant and the acidity shows that
the particle of the sulfuric acid is not contained in the
activated complex and that the formation of the alkyl acid

Card 2/3   belongs to the first order. Finally, an expression for the

SOV/2o-121-6-24/45

The Velocity of the Absorption of Ethylene and Propylene by Sulfuric Acid of Various Concentrations

velocity of the alkylation reaction is given and explained. There are 1 figure, 1 table, and 8 references, 5 of which are Soviet.

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR
(Institute of Chemical Physics,AS USSR)

PRESENTED: April 24, 1958, by V. N. Kondrat'yev, Academician

SUBMITTED: April 22, 1958

Card 3/3

5(4), 5(3)

AUTHORS: Kudryavtseva, T. A., Chirkov, N. M.   SOV/76-32-10-2/39

TITLE: The Kinetics of the Reaction of the Chlorine Exchange in Iso-
                meric β-Chlorocrotonic Acids I (Kinetika reaktsii obmena
                khlora v izomernykh β-khlorkrotonovykh kislotakh I)

PERIODICAL: Zhurnal fizicheskoy khimii, 1958, Vol 32, Nr 10, pp 2236-2241
                (USSR)

ABSTRACT: The exchange mechanism of a halogen atom bound to a carbon atom
                (with a multiple bond) has not been investigated in detail as
                yet. The problem of the influence of the configuration of un-
                saturated compounds on the movability of the halides seems to
                be especially interesting. The interaction of carbonyl groups
                with the chlorine atom leads to a coupling of two single bonds
                by way of a double bond, called δ-δ-coupling by A. N. Nesmeyanov
                (Ref 3). Nesmeyanov assumed that for this coupling a parallel
                direction of the bonds to be coupled was essential. The
                structural formula of the trans-β-chlorocrotonic acid and that
                of the cis-isomers show that the bonds CO-C and C-Cl are
                parallel in the first case, and that they are at an angle to
Card 1/3   each other in the isomer. From this it might be concluded that

SOV/76-32-10-2/39

The Kinetics of the Reaction of the Chlorine Exchange in Isomeric β-Chloro-crotonic Acids I

the mobility of the chlorine atom in the trans-isomer has to be greater than that of the cis-isomer. As this can only be found out by the kinetic method, the latter was also employed in this work. The measurements of the reaction kinetics were carried out in water-alkaline solutions of definite concentrations and at different temperatures. From the kinetic curves obtained it may be seen that the trans-isomer reacts much more rapidly than the cis-isomer. The values of the reaction constants (trans-isomer $5,48.10^{10}$, and cis-isomer $5,48.10^9$) show that the trans-β-chlorocrotonic acid reacts at any temperature ten times more rapidly than the cis-isomer. The values of the activation energy are the same for either of the isomers ($21,3\pm0,2$ kcal/mol). The difference in the reaction velocity is explained by the influence of electric steric factors. After the present paper had been completed information was received (Ref 6) on investigations of the chlorine exchange with assumptions in contradiction to the data given here. Those assumptions are counter-proved with reference to the value of the activation energy that remains the same. There are 4 figures, 3 tables, and 6 references, 2 of which are Soviet.

Card 2/3

SOV/76-32-10-2/39

The Kinetics of the Reaction of the Chlorine Exchange in Isomeric β-Chloro-crotonic Acids I

ASSOCIATION: AN SSSR, Institut khimicheskoy fiziki, Moskva (Moscow, Institute of Chemical Physics, AS USSR)

SUBMITTED: July 11, 1956

Card 3/3

CHIRKOV, N.M.

[Acid heterogeneous catalysis; abstract of a dissertation for
the degree of Doctor of Chemical Sciences] O kislotnom getero-
gennom katalize; avtoreferat dissertatsii na soiskanie uchenoi
stepeni doktora khimicheskikh nauk. Moskva, Akad.nauk SSSR,
1958. 15 p.   (MIRA 12:9)

        (Catalysis)

SOV/76-33-2-3/45

5(4)
AUTHORS: Kudryavtseva, T. A., Chirkov, N. M.

TITLE: Reaction Kinetics of Chlorine Exchange in Isomeric β-Chloro-
crotonic Acids (Kinetika reaktsii obmena khlora v izomernykh
β-khlorkrotonovykh kislotakh). II. Reaction of the Chlorine
Exchange With Lye in Alcohol Solutions (II. Reaktsiya ob-
mena khlora so shcheloch'yu v spirtovykh rastvorakh)

ABSTRACT: In a previous paper it was found (Ref 1) that the exchange
of the chlorine atom in cis and trans-β-chlorocrotonic
acids with the hydroxyl ion in aqueous medium occurs at
different rates, and that this is explainable not in terms
of energy factors but in terms of steric factors. Analogous
observations were made by Jones and Vernon (Dzhons)(Ref 2).
These observations were tested in the work reported here
using 50%, 75%, and pure methanol and ethanol. In the pure
alcohols β-ethoxy and β-methoxy crotonic acids were ob-
tained, since the chlorine atom is replaced by the alkoxyl
ion instead of by the hydroxyl ion. The experiment involved

Card 1/3

Reaction Kinetics of Chlorine Exchange in Isomeric   SOV/76-33-2-3/45
β-Chlorocrotonic Acids. II. Reaction of the Chlorine Exchange With Lye
in Alcohol Solutions

adding alcohol to weighed portions of the crotonic acid
isomers in a thermostat, warming, adding 20% sodium hydro-
xide, and then determining by the Volhard (Vol'gard) method
the chloride ion in samples removed at definite intervals.
The kinetic curves for the reaction in 75% ethanol (Fig 1)
show that the trans isomer reacts more quickly than the
cis isomer, and that the reaction is irreversible and bi-
molecular. The rate constants, calculated from the equation
for irreversible bimolecular reactions (Tables 1,2), allow
the activation energy to be determined; for the cis isomer
this was found to be 20.3 and for the trans isomer
20.8 kcal/mol. For the 50% ethanol an average value (for
both isomers) of 21.4±0.5 kcal/mol was found. In the 50%
and 75% methanol only the cis isomer was investigated;
activation energies of 22.8 kcal/mol and 21.5 kcal/mol
were found. The difference in reaction rates was here also
attributed to steric factors, since a difference in the
Card 2/3   pre-exponents appears (especially in diluted alcohol solutions)

Reaction Kinetics of Chlorine Exchange in Isomeric   SOV/76-33-2-3/45
β-Chlorocrotonic Acids. II. Reaction of the Chlorine Exchange With Lye
in Alcohol Solutions

while the activation energies for both isomers are almost
equal. A maximum difference of 12.5 times was observed
between the rates of reaction, although this decreased to
a factor of 1.5 with an increase in the alcohol concentration.
There are 5 figures, 6 tables, and 3 references, 1 of which
is Soviet.

ASSOCIATION: Akademiya nauk SSSR, Institut khimicheskoy fiziki, Moskva
              (Academy of Sciences, USSR, Institute of Chemical Physics,
              Moscow)

SUBMITTED: March 15, 1957

Card 3/3

5 (4)

AUTHORS: Manelis, G. B., Vinnik, M. I.,   SOV/76-33-5-11/33
             Chirkov, N. M. (Moscow)

TITLE: The Acid Function of the System Diethyl Ether - BF_3

             (Funktsiya kislotnosti sistemy dietilovyy efir - BF_3)

ABSTRACT: The acid function was investigated over a wide concentration
             range by using various indicators: 2,4-dinitroaniline, 2,4-
             dichloro-6-nitroaniline, 5-Cl-2-nitroaniline, and o-nitro-
             aniline. The measurement was carried out by means of the
             spectrophotometer SF-4 at room temperature. The compound
             $(C_2H_5)_2OBF_3$ was synthesized in a quartz cuvette. Table 1

             shows the dependence of $\lg \dfrac{C_B}{C_{BH^+}}$ on the concentration of the

             ether compound for the individual indicators (C_B = concentration
             of the non-ionized indicator, C_{BH}^+ = concentration of the

Card 1/3   ionized indicator). The determination of the acid function

The Acid Function of the System Diethyl Ether - BF$_3$ SOV/76-33-5-11/33

was carried out assuming that the ether compound investigated is a strong acid and that indicators in strong acids have the same value of pK$_B$ (negative logarithm of the basicity constant). Therefore, pK$_B$ = -4.4 was put for 2,4-dinitroaniline, and pK$_B$ for the other indicators determined by the usual method. The possible inaccuracies of the determination are discussed. Table 2 and a figure give the results of the determination. The reasons for the deviation of the data obtained from the results mentioned in reference 3 could not be found. Starting from the equilibrium constant the equation of the acid function for $(C_2H_5)_2OBF_3$ in $(C_2H_5)_2O$ is deduced:

$$H_0 = \lg \sqrt{k_1\left(\frac{100}{[AH]} - 1\right) + k_2}$$

$(C_2H_5)_2OBF_3$ surpasses the phosphoric acid because of its acidity degree (H_0 = -6.22 at 100°). The quantitative data of the polymerization rate of isobutylene are in good agreement with it. There are 1 figure, 2 tables, and 7 references, 5 of which are Soviet and 1 Czechoslovakian.

Card 2/3

The Acid Function of the System Diethyl Ether - BF_3 SOV/76-33-5-11/33

ASSOCIATION: Akademiya nauk SSSR Institut khimicheskoy fiziki Moskva
                 (Academy of Sciences of the USSR, Institute of Chemical
                 Physics, Moscow)

SUBMITTED: October 9, 1957

Card 3/3

· 5(4)

SOV/76-33-6-37/44

AUTHORS: Kazanskiy, K. S., Entelis, S. G., Chirkov, N. M.

TITLE: Solubility of Gaseous Isobutylene in Water (Rastvorimost'
              gazoobraznogo izobutilena v vode)

PERIODICAL: Zhurnal fizicheskoy khimii, 1959, Vol 33, Nr 6,
              pp 1409-1413 (USSR)

ABSTRACT: The solubility of isobutylene (I) in water (0 - 70°C) and
              aqueous NaCl-solutions (0 to - 5°C) at 1 atm pressure was
              investigated. The quantity of dissolved (I) was determined
              by the pressure drop in an accurately measured gas volume
              as in the experiments (Ref 2). The vessel (Fig 1), in which
              the measurements were made, had an oblong shape, and was
              placed, during the measurements, into a thermostat, where
              the intermixture was effected by shaking. The Henry constant
              was computed from the experimental results by an equation (3)
              (Table 1), and it was ascertained that the heat of solution
              ΔH_s rises with a reduction of temperature. The experimental
              results obtained -- in contrast to other publication references

Card 1/3   on the water solubility of gases -- cannot be described by

Solubility of Gaseous Isobutylene in Water

SOV/76-33-6-37/44

the classic equation according to Valentiner (Ref 6). In the temperature interval 70 - 25°C, ΔH_s is constant and amounts to 4620 $\pm$ 40 cal/mol; a further reduction of temperature leads to a rise of the heat of solubility (Fig 3). It is assumed that in the (I)-dissolution in water, two processes go on in parallel - one can be regarded as a physical disintegration, the other as a formation of an (I)-hydrate - so that the solubility as a function of temperature can be expressed by the sum of two exponential quantities (Equation (6)). The determination of the Henry constant for (I) in NaCl-H_2O mixtures at 0°C (Table 2) and -5°C (Table 3) shows that at -5°C the equation according to Sechenov cannot be applied. There are 4 figures, 3 tables, and 10 references.

ASSOCIATION: Institut khimicheskoy fiziki
             (Institute of Chemical Physics)
Card 2/3

SOV/76-33-6-37/44

Solubility of Gaseous Isobutylene in Water

SUBMITTED: December 27, 1957

Card 3/3

SOV/76-33-9-17/37

5(4)
AUTHORS: Vinnik, M. I., Ryabova, R. S., Chirkov, N. M.

TITLE: Kinetics and Mechanism of Reactions in Concentrated Strong Acid Media. I. Kinetics of Dehydration of o-Benzoyl Benzoic Acid in Concentrated Solutions of Sulphuric Acid

PERIODICAL: Zhurnal fizicheskoy khimii, 1959, Vol 33, Nr 9, pp 1992-2001 (USSR)

ABSTRACT: An investigation was made of the kinetics of catalytic dehydration of o-benzoyl benzoic acid (I) to anthraquinone in sulphuric acid (79.92% to 100%) at temperatures of from 50° to 97.5°C. The spectrophotometrical method (spectrophotometer type SF-4) was applied and the dependence of the dehydration rate constant on the acidity of the medium and on temperature was determined (Table 1). Three forms of (I) were found to occur in the state of equilibrium in the case of (I) being ionized in highly acid medium - a non-ionized form BOH, a protonized form BOH$^+$, and a dehydrated protonized form B$^+$. The ratio between the concentrations of the three forms is determined by the acidity of the medium and the activity of water. The limiting stage of the process is the isomerization of the dehydrated

Card 1/3

Kinetics and Mechanism of Reactions in Concentrated Strong Acid Media. SOV/76-33-9-17/37
I. Kinetics of Dehydration of o-Benzoyl Benzoic Acid in Concentrated Solutions
of Sulphuric Acid

form B^+. A specification is given of the values of the actual
rate constants at $25^\circ C$, as obtained by extrapolation (according
to the Arrhenius Law), further, the concentration of the three
forms of (I) at various sulphuric acid concentrations (Table 2),
as well as the dependence of the ionization constant on acidity
(Table 3). By spectrometric and kinetic methods the following
values were obtained:

$$K_1 = \frac{a_{H^+} \, a_{BOH}}{a_{BOH_2^+}} = 4 \cdot 10^8; \quad K_2 = \frac{a_{H^+} \, a_{BOH_2^+}}{a_{B^+} \, a_{H_3O^+}} = 1 \cdot 10^9$$

Values were obtained for the true activation energy
$E_W = 24.5$ kcal/mol (characteristic of the energy balance of
the elementary act of the isomerization of dehydrated (I)-ion
to anthraquinone), the sum of the ionization heats
$Q_1 + Q_2 = 6.5$ kcal/mol, and the value of the true preexponential
factor $A = 7 \cdot 10^{11}$ sec^{-1}. There are 7 figures, 3 tables, and

Card 2/3

Kinetics and Mechanism of Reactions in Concentrated Strong Acid Media.   SOV/76-33-9-17/37
I. Kinetics of Dehydration of o-Benzoyl Benzoic Acid in Concentrated Solutions
of Sulphuric Acid

8 references, 1 of which is Soviet.

ASSOCIATION: Akademiya nauk SSSR,Institut khimicheskoy fiziki,Moskva
(Academy of Sciences of the USSR, Institute of Chemical
Physics, Moscow)

SUBMITTED: February 22, 1958

Card 3/3

5(4)

AUTHORS: Tsvetkova, V. I., Firsov, A. P.,   SOV/20-124-1-39/69
   Chirkov, N. M.

ABSTRACT: In acid-catalytic transformations the basicity of the molecules
            of the reagent and the reactivity of the protonized forms are
            the most important factors that influence the course taken by
            reactions. Investigation of these factors is one of the main
            problems in the theory of acid catalysis. Previous papers
            dealing with this subject are dealt with in short. Works
            hitherto carried out in connection with the reactivity of
            alcohols have, according to the authors' opinion, the
            disadvantage that reaction rates are compared at different
            concentrations of the reacting particles. In order to avoid
            this mistake, the authors chose solutions of HCl in waterless
            alcohols as experimental objects. In these solutions only the
Card 1/4   solutions of alcohol are, of course, protonized. In the case

The Determination of the True Constant of Rates in the SOV/20-124-1-39/69
Decomposition of Aliphatic Alcohols

of sufficient dilution, the HCl-molecules are nearly totally dissociated, and therefore the concentration of the ions of alcoxonium (alkoksoniy) will in practice be equal to the stoichiometric concentration of the acid. Under the conditions prevailing in this case, only alkyl-halides are formed by the dehydration of the alcohols as end products. The reactions occurring in the systems investigated can be described by the scheme $ROH + HCl \rightleftarrows ROH_2^+Cl^- \rightleftarrows ROH_2^+ + Cl^-$. In diluted solutions equilibrium is shifted to the right. It further holds that

$$ROH_2^+ \xrightarrow{k_1} R^+ + H_2O \text{ (slow)}, \quad R^+ + Cl^- \longrightarrow RCl \text{ (fast)},$$
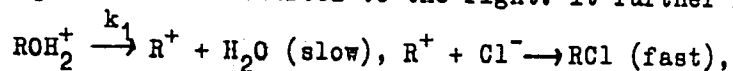
$$ROH_2^+ + Cl^- \xrightarrow{k_2} RCl + H_2O.$$ The following aliphatic alcohols were used for experimental purposes: ethyl-n-propyl-alcohol, i-propyl-alcohol, n-butyl-alcohol, i-butyl-alcohol, and tertiary butyl alcohol. The investigation was carried out at $65 - 95°$ and at various initial concentrations of the HCl (from 0.03 to 1.5N) by means of the usual ampoule method. A

Card 2/4

The Determination of the True Constant of Rates in the   SOV/20-124-1-39/69
Decomposition of Aliphatic Alcohols

table by way of example shows the results for n-butyl-alcohol.
Analogous results were obtained also for other alcohols
investigated in this connection. With the investigated
experimental conditions prevailing, the monomolecular
mechanism predominates. For various alcohols a diagram
shows the dependence of the constants found on the temperature
for the initial HCl concentration ~0.03. The activation energies
of most of the alcohols investigated did not differ essentially
from one another. Only in the case of isobutyl-alcohol
activation energy is considerably lower. It may be that in this
case the reaction develops according to another and more
complicated mechanism, and the values found for the constants
perhaps do not correspond with the true values. The considerable
differences between alcohol dehydration rates in aqueous acid
solutions are essentially determined by their different
degree of protonization. There are 1 figure, 2 tables, and
13 references, 6 of which are Soviet.

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR (Institute
Card 3/4   for Chemical Physics of the Academy of Sciences, USSR)

5(4)

AUTHORS: Utyanskaya, E. Z., Stepanyants, A. U.,   SOV/20-124-5-38/62
            Vinnik, M. I., Chirkov, N. M.

TITLE: The Calculation of the Function of Acidity and the Molecular
            Composition of Hydrofluoric Acid From the Data of the Nuclear
            Magnetic Resonance of F^{19} (Raschet funktsii kislotnosti i
            molekulyarnogo sostava plavikovoy kisloty po dannym yadernogo
            magnitnogo rezonansa F^{19})

ABSTRACT: Hammett's function of acidity is measured by means of the indi-
            cator method and amounts to $H_0 = -\lg a_{H+}(f_B/f_{BH+})$. Here f_B
            and f_{BH+} denote the coefficients of the activities of the
            ionized and not ionized forms of the indicator; a_{H+} - the proton
            activity in the given medium. In the aqueous solutions of HF
            there are the following kinds of equilibrium: $HF \rightleftharpoons H^+ + F^-$ (2);
            $HF + F^- \rightleftharpoons HF_2^-$ (3); $K_1 = a_{H+}a_{F^-}/a_{HF}$ (4); $K_2 = a_{HF_2^-}/a_{HF}a_{F^-}$ (5).

Card 1/3

The Calculation of the Function of Acidity and the   SOV/20-124-5-38/62
Molecular Composition of Hydrofluoric Acid From the Data of the Nuclear
Magnetic Resonance of F^{19}

Here $K_1 = 6.89 \cdot 10^{-4}$ and $K_2 = 2.695$ denote the constants
of equilibrium, expressed in activities. From the dissociation
equation (4) of hydrofluoric acid there follows:
$-lg \, a_{H^+} = -lg \, K_1 + lg \, (a_{F^-}/a_{HF})$. If the quantities K_1, a_{HF},
and m_{F^-} are known, it is possible to calculate the acidity
function $\mathcal{H}_0$. For the purpose of determining quantitative re-
sults concerning the composition and the acidity of concen-
trated aqueous solutions of HF the authors carried out
measurements of the chemical shifts of the resonance of F^{19}
in aqueous solutions of hydrofluoric acid of different concen-
trations. For the chemical shift to be observed and also for
a system consisting of several interacting components expres-
sions are written down. The chemical shift to be observed is
of the order of magnitude $(5.95 \text{ to } 6.05) \cdot 10^{-4}$ for the
various concentrations of hydrofluoric acid. In order, therefore
to be able to determine the acidity function with an accuracy

Card 2/3

The Calculation of the Function of Acidity and the   SOV/20-124-5-38/62
Molecular Composition of Hydrofluoric Acid From the Data of the Nuclear
Magnetic Resonance of F^{19}

of ± 0.05, it is necessary to know the observable chemical
shift with an accuracy of $\pm 0.03 \cdot 10^{-4}$. Measurements were carried
out in a magnetic field of ~3,300 oersted. In the course of
these measurements a saw-tooth modulation of the magnetic main
field was used. The results obtained by measurements are shown
by a table and by a diagram. At concentrations of up to 30 %
the variations of the chemical shift are within the limits of
measuring errors. The results obtained by calculating molecular
composition and the acidity function are shown by tables and
diagrams. There are 4 figures, 2 tables, and 9 references,
5 of which are Soviet.

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR (Institute
                of Chemical Physics of the Academy of Sciences, USSR)

PRESENTED: October 29, 1958, by V. N. Kondrat'yev, Academician

SUBMITTED: October 22, 1958

Card 3/3

5(4)

AUTHORS: Vinnik, M. I., Zarakhani, N. G., Medvetskaya, I. M.,
           Chirkov, N. M.

TITLE: The Role of Salt Formation in Acid-catalytic Processes. The
           Kinetics of Cyclohexanone Oxime Hydrolysis (O roli soleobrazo-
           vaniya v kislotno-kataliticheskikh protsessakh. Kinetika
           gidroliza tsiklogeksanonoksima)

ABSTRACT: The hydrolysis of amides and oximes is accelerated by acids
            and bases. An anomalous dependence of the reaction rate upon
            the acidity of the medium is observed in acid hydrolysis
            (Refs 1-4). The value of the reaction constant increases with
            increasing HCl-concentration up to a certain amount and then
            decreases again. An investigation of the bimolecular reaction
            between the "protonized" molecule of the reagent and water :

$$RCONH_2 + H^+ \rightleftarrows RCONH_3^+ \; ; \; RCONH_3^+ + H_2O \rightleftarrows M^* \xrightarrow{k} \quad product$$

            of hydrolysis shows that this reaction is not able to explain
            the phenomena observed. The authors assume that the "protonized"
Card 1/2   form of the reagent is able to combine with the acid anion to a

The Role of Salt Formation in Acid-catalytic Processes. SOV/20-126-6-43/67
The Kinetics of Cyclohexanone Oxime Hydrolysis

non-dissociated salt. In order to prove the rightness of this assumption, the hydrolysis of cyclohexanone oxime was spectrophotometrically investigated at λ = 222 mμ under the catalytic effect of hydrochloric acid. A kinetic curve is derived (Fig 1) under consideration of a monomolecular reaction of the hydrolysis of the oxime and (in the case of a reverse process) of the bimolecular oxime formation from cyclohexanone and hydroxylamine. Table 1 and figure 2 show the experimental results and confirm that the reaction constant of hydrolysis passes through a maximum. A decreasing rate of hydrolysis (Table 2) was brought about by experiments made with the addition of NaCl and LiCl. Therefore, salt formation inhibits acid catalytic processes by reducing the concentration of the reactive form of the reagent. In the hydrolysis of cyclohexanone oxime, the stage of isomerization of the "protonized" form has a limiting effect. There are 2 figures, 2 tables, and 7 references, 2 of which are Soviet.

PRESENTED: February 26, 1959, by V. N. Kondrat'yev, Academician

SUBMITTED: February 20, 1959
Card 2/2

'5 (2)

AUTHORS: Kudryavtseva, T. A., Chirkov, N. M.,   SOV/20-127-1-28/65
             Kochetkov, N. K.

TITLE: The Reaction Kinetics of a Nucleophilic Substitution of Chlo-
             rine in Phenyl-β-chlorovinyl-ketone (Kinetika reaktsii nukleo-
             fil'nogo zameshcheniya khlora v fenil-β-khlorvinilketone)

ABSTRACT: The   published data on the reaction at the unsaturated carbon
             atom mentioned in the title is very rare. The halogen atom at
             the carbon with a double bond in compounds of the chlorovinyl-
             ketone type is known to be very inert in substitution reactions.
             It gets, however, unstable and enters easily into the afore-
             mentioned reaction if the other side of the double bond is an
             electrophilic group (CO, COOH, COOR etc.) (Refs 1,2). Since the
             hitherto existing data were merely qualitative, no comparison
             was possible of the mobility of the halogen with respect to the
             type of the activating groups (CO, COOH, COOR etc.) as well as
             with respect to the type of the attacking nucleophilic reagent.
             The kinetic data necessary for this purpose was obtained in the
Card 1/3   laboratory of the institute mentioned in the Association (Ref 3);

the topic mentioned in the title was investigated as its con-
tinuation. The above substance is known to be a trans-isomer
(Ref 4). Its solution (in absolute ether) was mixed with a
solution of sodium ethylate (in excess). Methyl alcohol served
as a thermostat. Figure 1 shows the resultant kinetic curves.
The velocity constants calculated from the latter (by the for-
mula for irreversible bimolecular reaction) were practically
constant. Table 1 shows that the doubling of the initial con-
centration of sodium ethylate changed the reaction velocity as
was expected, the values of the above-mentioned constants re-
mained nevertheless the same. The pre-exponential member $K_o =$

$= 4 \cdot 10^7$ was too low by three orders of magnitude compared with
a normal one for a bimolecular reaction (Table 2). This indi-
cates that the reaction is in this case in fact bimolecular
(as well as in the case of β-chloro-crotonic acids, Ref 3).
Thus, the type of the activating groups does not influence the
exchange reaction order of halogen substitution in compounds
of the type of β-substituted halogen vinyls. The type of this
group influences, however, considerably the exchange rate of

Card 2/3

The Reaction Kinetics of a Nucleophilic Substitution SOV/20-127-1-28/65
of Chlorine in Phenyl-β-chlorovinyl-ketone

the halogen atom, i.e. the activation energy (see Scheme p
108). There are 2 figures, 2 tables, and 5 references, 4 of
which are Soviet.

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR (Institute of
Chemical Physics of the Academy of Sciences, USSR)

PRESENTED: March 9, 1959, by V. N. Kondrat'yev, Academician

SUBMITTED: March 3, 1959

Card 3/3

CHIRKOV, N.M.

Mechanism of homogeneous acid catalysis and its relation to
heterogeneous acid catalysis. Probl. kin. i kat. 10:255-272 '60.
(MIRA 14:5)

1. Institut khimicheskoy fiziki AN SSSR.
             (Catalysis) (Acids)

VINNIK, M.I.;   MANELIS, G.B.;   CHIRKOV, N.M.

Catalytic properties of complex compounds of boron fluoride. Probl.
kin. i kat. 10:285-290 '60.   (MIRA 14:5)

1. Institut khimicheskoy fiziki AN SSSR.
                        (Boron fluoride)

ENTELIS, S.G.; KOROVINA, G.V.; CHIRKOV, N.M.

Acidity function of solutions of propylene in aqueous sulfuric
acid. Izv. AN SSSR.Otd. khim. nauk no.11:2050-2052 N '60.
(MIRA 13:11)

1. Institut khimicheskoy fiziki AN SSSR.
    (Propene) (Sulfuric acid)

ENTELIS, S.G.; KOROVINA, G.V.; CHIRKOV, N.M.

Thermodynamic activity of water in the system $H_2O - H_2SO_4 - 1-C_3H_7OH$
Izv.AN SSSR.Otd.khim.nauk .no.12:2252-2254 D '60.
(MIRA 13:12)

1. Institut khimicheskoy fiziki AN SSSR.
(Activity theory)   (Sulfuric acid)   (Isopropyl alcohol)

6/4300

68853

AUTHORS: Kudryavtseva, T. A., Chirkov, N. M.

S/076/60/034/02/017/044
B010/B017

TITLE: Reaction Kinetics of Chlorine Exchange in Isomeric β-Chlorocrotonic Acids. III. Reaction of Chlorine Exchange With Alkoxy Groups

PERIODICAL: Zhurnal fizicheskoy khimii, 1960, Vol 34, Nr 2, pp 375-379 (USSR)

ABSTRACT: For the purpose of solving the problem of the mobility of chlorine in unsaturated compounds, β-chlorocrotonic acids were chosen since the geometric isomers of the latter can be easily produced in a pure form. The reaction rate of the chlorine substitution in sodium salts of the cis- and trans-β-chlorocrotonic acids with alkoxy ions was investigated under the action of sodium ethylate, -phenolate, and -benzylate in absolute ethanol. The samples were taken at certain intervals, and chlorine was determined according to Volhard. The reaction rate was determined at various initial concentrations of the reagents and various temperatures, and the kinetic curves were drawn. The dependence of the reaction rate on temperature is given (Tables 1-3), as well as the values of the coefficients of the exponential function and the activation energies of the individual pairs of isomers (Table 4). The reactions investigated are irreversible and bimolecular. As had been expected the trans-isomers reacted more rapidly than the cis-isomers.

Card 1/2

Reaction Kinetics of Chlorine Exchange in Isomeric
β-Chlorocrotonic Acids. III. Reaction of Chlorine
Exchange With Alkoxy Groups

68853
S/076/60/034/02/017/044
B010/B017

The activation energy for each pair of isomers is about 23 kcal/mol.
The difference in the reaction rate of the isomers is expressed by
the coefficient of the exponential function, i.e. it is explained
by steric obstacles. With respect to their activity, the reagents
investigated can be set up in the following order according to their
nucleophilic properties: benzylate, ethylate, phenolate. The sta-
bility of the compounds newly formed in the substitution reaction
does not influence the activation energy, increases, however, the
probability of formation of an intermediate complex. There are 2
figures, 4 tables, and 6 references, 2 of which are Soviet.

ASSOCIATION: Akademiya nauk SSSR Institut khimicheskoy fiziki (Academy of
              Sciences of the USSR, Institute of Chemical Physics)

SUBMITTED: May 9, 1958

Card 2/2

KUDRYAVTSEVA, T.A.; CHIRKOV, N.M. (Moscow)

Kinetics of chlorine exchange in isomeric β-chlorocrotonic
acids. Part 4: Exchange of chlorine with sodium benzilate
in esters of cis- β-chlorocrotonic acid.   Zhur.fiz.khim.
34 no.6:1307-1311 Je '60.   (MIRA 13:7)

1. Akademiya nauk SSSR, Institut khimicheskoy fiziki.
        (Crotonic acid) (Chlorine) (Benzilic acid)

AUTHORS: Tsvetkova, V. I.,   Firsov, A. P., and Chirkov, N. M.

TITLE: Determination of the True Constants of the Decay Rate of
             Alkoxonium Ions in the Interaction Between Aliphatic
             Alcohols and Hydrogen Chloride

PERIODICAL: Zhurnal fizicheskoy khimii, 1960, Vol. 34, No. 9,
             pp. 2066-2074

TEXT: It was the purpose of the present work to determine the true
constants of the decomposition rate of alkoxonium ions of a series of
aliphatic alcohols: ethyl-, n-propyl-, isopropyl-, n-butyl-, iso-butyl-,
and tert-butyl alcohol, and thus also of the reactivity of these ions.
For this purpose, the formation rate of alkyl halides for HCl-solutions
in water-free alcohols was investigated, viz. at various HCl-concentra-
tions (from 0.03 to 1.5 N) in the temperature interval of from 65 to
95°C. The investigations were carried out in ampoules which had been
placed into a liquid thermostat, whose temperature was kept constant
with an accuracy of $\pm 0.2^{\circ}$. For titration, a 0.02516 N NaOH-solution

Card 1/4

Determination of the True Constants of the   S/076/60/034/009/032/041XX
Decay Rate of Alkoxonium Ions in the Inter-   B020/B056
action Between Aliphatic Alcohols and Hydrogen
Chloride

was used; the indicator used was methyl red. Mainly the dependence of
the formation rate of alkyl halides on the initial concentration of
the HCl in water-free alcohols as well as the temperature dependence
of the reaction rate were investigated. The results obtained for HCl
solutions in ethyl-, n-propyl-, iso-propyl-, n-butyl-, and isobutyl
alcohol are given in Tables 1-6. In these tables the rate constant values
k_1 calculated from the equation of the monomolecular reaction at various
temperatures and different initial concentrations of HCl, the calculat-
ed values of the factors of the exponential functions k_0, and the acti-
vation energies E are given. The character of the relation between the
formation rate of the alkyl halide and the initial HCl concentration
is complicated. Table 7 gives the values of monomoleular constants for
70°, the factors of the exponential function, and the activation ener-
gies, as well as of the decomposition of the protonized molecules of
various alcohols. The values k_1, k_0, and E found for isobutyl alcohol

can, however, not be considered to be characteristic of the decay rate

Card 2/4

Determination of the True Constants of the   S/076/60/034/009/032/041XX
Decay Rate of Alkoxonium Ions in the Inter-   B020/B056
action Between Aliphatic Alcohols and Hydrogen
Chloride

of the iso-$C_4H_9OH_2^+$-ions. From the data found it follows that the fac-
tors of the exponential functions for the ion decay $C_2H_5OH_2^+$, $C_3H_7OH_2^+$,

$C_4H_9OH_2^+$, $(CH_3)_2CHOH_2^+$, and $(CH_3)_3COH_2^+$ have values of from

$2.8 \cdot 10^{12}$ to $2.5 \cdot 10^{14}$ sec^{-1}, i.e., that lie near the theoretical value
for monomolecular reactions. The activation energies of the decay of
these ions are within the range of from 28,000 to 31,000 cal/mole
(Table 7). At the same temperature, the values of the rate constants
for the investigated alcohols differ by no more than the tenfold
(cf. Table 7). The great differences found for the rates in the dehydra-
tion of the alcohols by means of aqueous acid solutions, cannot be
explained solely by the different reactivity of the protonized alcohol
molecules, but is, in a high degree, determined by the different basici-
ty of the alcohols, i.e., by the parameters of thermodynamic, not
kinetic, character. There are 7 tables and 18 references: 7 Soviet,
3 US, 6 British, and 2 German.
Card 3/4

Determination of the True Constants of the   S/076/60/034/009/032/041XX
Decay Rate of Alkoxonium Ions in the Inter-   B020/B056
action Between Aliphatic Alcohols and Hydrogen
Chloride

ASSOCIATION: Akademiya nauk SSSR, Institut khimicheskoy fiziki
                (Academy of Sciences of the USSR, Institute of Chemical
                Physics)

SUBMITTED: January 5, 1959

Card 4/4

S/020/60/132/05/49/069
B004/B011

AUTHORS: Entelis, S. G., Kazanskiy, K. S., Chirkov, N. M.

TITLE: γ Thermodynamics of Isobutylene Protonization γ

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol. 132, No. 5,
             pp. 1152-1155

TEXT: The authors wanted to make a direct determination of the equilib-
rium constants of olefin protonization, as well as of the heat and entropy
of this reaction. They investigated the system isobutylene – sulfuric
acid – water in which connection the conversion of iso-C_4H_8 in the liquid
phase was measured spectrophotometrically at 210 mμ (Fig. 1). In order
to obtain measurable reaction rates, it was necessary to work at -15 to
-35°C. Fig. 2 shows the dependence of log D_{210} on the reaction time τ
(D_{210} = optical density at 210 mμ). Fig. 3 illustrates the dependence of
the molar extinction coefficient ε on temperature. The basicity constant pK

$\sqrt{B}$

Card 1/3

Thermodynamics of Isobutylene Protonization   S/020/60/132/05/49/069
B004/B011

was calculated (Table 1) whose dependence on $1/T$ is shown in Fig. 4. The heat $\Delta H_R = 4.3 \pm 4$ kcal/mole was found for the protonization of iso-C_4H_8, and $\Delta S = +8.20$ e.u. for the entropy. Moreover, the value for $\Delta H_s(\text{tert-}C_4H_9^{\bullet})$ equal to (-64 ± 4) kcal/mole was calculated from equation

(8) $\Delta E_s(\text{tert-}C_4H_9^{\bullet}) + \Delta H_s(H_2O) - \Delta H_s(\text{iso-}C_4H_8) - \Delta H_s(H_3O^{\oplus}) = 33$ kcal.

The authors discuss the paper by V. N. Kondrat'yev and N. D. Sokolov (Ref. 7). They assume two types of interaction of the carbonium ion with water: solvation, or donor-acceptor interaction under the formation of an alkoxonium ion, which two interactions are separated by a potential barrier. The authors refer to a paper by A. I. Gel'bshteyn, G. G. Shcheglova, and M. I. Temkin (Ref. 3). There are 4 figures, 1 table, and 8 references: 4 Soviet, 3 British, and 1 American.

ASSOCIATION: Institut khimicheskiy fiziki Akademii nauk SSSR (Institute of Chemical Physics of the Academy of Sciences, USSR)

V/B

Card 2/3

Thermodynamics of Isobutylene Protonization   S/020/60/132/05/49/069
                                                B004/B011

PRESENTED: January 19, 1960, by V. N. Kondrat'yev, Academician

SUBMITTED: January 15, 1960

✓B

Card 3/3

ENTELIS, S.G.; KOROVINA, G.V.; CHIRKOV,N.M.

Thermodynamics of the absorption of propylene by the system H_2SO_4 - H_2O. Dokl.AN SSSR 134 no.4:856-859 O '60.

(MIRA 13:9)

1. Institut khimicheskoy fiziki Akademii nauk SSSR. Predstavleno akad. V.N.Kondrat'yevym.
    (Propene)   (Sulfuric acid)

TSVETKOVA, V.I.; PIROGOV, O.N.; LISITSYN, D.M.; CHIRKOV, N.M.

Kinetics and mechanism of olefin polymerization on complex catalysts.
Part 1: Kinetic equations and determination of the rate constants
for the polymerization of α-olefins on the system $TiCl_3$ - AlR_3 when
different methods of accomplishing the process are employed. Vysokom.
soed. 3 no.4:585-593 Ap '61.   (MIRA 14:4)

1. Institut khimicheskoy fiziki AN SSSR.
          (Olefins)   (Polymerization)

ENTELIS, S.G.; KONDRAT'YEVA, G.P.; CHIRKOV, N.M.

Kinetics and mechanism of the initial stage of the polycondensation
of terephthaloyl chloride with ethylene glycol. Part 1: Relation
between the reaction rate and the polarity of the medium. Vysokom.
soed. 3 no.1044-1053 Jl '61.   (MIRA 14:6)

1. Institut khimicheskoy fiziki AN SSSR.
   (Terephthaloyl chloride) (Ethylene glycol) (Polymerization)

26293

S/190/61/003/008/006/019
B110/B220

IS.8610

AUTHORS: Firsov, A. P., Tsvetkova, V. I., Chirkov, N. M.

TITLE: Kinetics and mechanism of the polymerization of α-olefins by complex catalysts. II. Polymerization of propylene in the presence of titanium trichloride and various aluminum alkyl compounds

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 3, no. 8, 1961, 1161-1169

TEXT: The polymerization of propylene in the system $TiCl_3$ + AlR_3 containing the following cocatalysts: $Al(C_2H_5)_3$, $Al(n-C_3H_7)_3$, $Al(i-C_4H_9)_3$; $Al(C_6H_5)_3$; $Al(C_2H_5)_2Cl$ was studied in order to clear up the mechanism of polymerization in this system. The experimental apparatus shown in Fig. 1 consisted of: reaction vessel 1, device 2 for introducing the catalyst components, burette 3 for introducing the solvent into the reaction vessel, device 4 for regulating the constant pressure of the propylene, manometer 5 regulating the gas pressure in the reaction vessel, and ЭПП-08 (EPP-08) recorder 6

Card 1/7

Kinetics and mechanism of the ...

26293
S/190/61/003/008/006/019
B110/B220

for recording the reaction rate based on the pressure of propylene, flask 7 for propylene, separating columns 8, and vacuum part 9. In order to dry the propylene obtained at 370°C by dehydration of isopropyl alcohol by means of Al_2O_3, it was passed through columns 8 filled with alkali, $Mg(ClO_4)_2$, and P_2O_5, and subsequently frozen by using liquid N_2. After the propylene had been thawed, the medium fraction was dried by Na wire. The alkyl halides were distilled twice. $TiCl_3$ was prepared according to

G. Brauer (Ref. 6: Rukovodstvo po preparativnoy neorganicheskoy khimii. (Manual of Preparative Inorganic Chemistry) Izd. in. lit., M., p. 547). Polymerization was performed at 40-70°C and at a propylene pressure of 170-300 mm Hg in the reaction vessel. The reaction rate was determined from the consumption of propylene. It was found that polymerization proceeds in two stages: a) unsteadily with increasing rate; b) steadily at a constant rate. The time $\tau_{1/2}$ needed for reaching half the steady rate is a function of pressure: $\tau_{1/2} = Q/p_{C_3H_6}$ (4). $\tau_{1/2}$ increases as follows:

$Al(n-C_3H_7)_3 < Al(C_2H_5)_3 < Al(iso-C_4H_9)_3$. The variation of the reaction rate

Card 2/7

Kinetics and mechanism of the ...

26293
S/190/61/003/008/006/019
B110/B220

is presumably due to the varying surface of the catalyst. The constants of the reaction rates are indicated in Table 1. The activation energy was almost constant within the experimental error: $E = 13,500 \pm 400$ cal/mole. The stereoisomeric composition of polypropylene is shown in Table 2. The following equation is derived for the constant k of the reaction rate:

$$k = \left[k_{incr}k_i/(k_{incr}/v + k_i)\right] S_{TiCl_3} c_o^*,$$ where k_{incr} is the constant of

increase; k_i is the constant of initiation; v is the polymerization degree; S_{TiCl_3} is the surface of $TiCl_3$; and c_o^* is the total number of active centers.

Provided that $k_i \gg k_{incr}/v$, k becomes equal to $A S_{TiCl_3} c_o^* \exp(-E_{incr}/RT)$.

The following values are indicated for the factor $A S_{TiCl_3} c_o^*$ in 1/min·g $TiCl_3$:

$Al(C_2H_5)_3$: $4.0 \cdot 10^6$; $Al(n-C_3H_7)_3$: $6.02 \cdot 10^6$; $Al(iso-C_4H_9)_3$: $3.15 \cdot 10^6$; $Al(C_6H_5)_3$: $0.9 \cdot 10^6$. The reaction rate is determined assuming that the polymerization is not effected by the growth of olefin molecules adsorbed

Card 3/7

Kinetics and mechanism of the ...

26293
S/190/61/003/008/006/019
B110/B220

on the catalyst but by dissolved olefin molecules colliding with the catalyst. The following is obtained per unit surface of $TiCl_3$, $70^\circ C$, $P_{C_3H_6}$ = 1 atm per second: $n = N_0 P/(2\pi MRT)^{1/2} = 2.2 \cdot 10^{23}$ $cm^{-2} \cdot sec^{-1}$

(N_0 = Avogadro number; p = pressure of propylene in bars; R = $8.31 \cdot 10^7$, n = number of collisions per cm^2 and sec). The reaction rate is $2.5 \cdot 10^{19}$ molecules/sec·g $TiCl_3$; S_{TiCl_3} = 5 m^2 per g of $TiCl_3$. The reaction rate observed for $k \cdot c_{C_3H_6}$ was $4.5 \cdot 10^{18}$ molecules/sec·g $TiCl_3$. Considering the approximative character of the calculation, the study is thought to be satisfactory. A. F. Popov is thanked for the AlR_3 compounds made available. There are 3 figures, 3 tables, and 9 references: 4 Soviet and 5 non-Soviet. The reference to English-language publications reads as follows: Ref 2: G. Natta, J. Polymer Sci., 34, 21-48, 1959.

ASSOCIATION: Institut khimicheskoy fiziki AN SSSR (Institute of Chemical Physics AS USSR)

Card 4/7

ENTELIS, S.G.; KONDRAT'YEVA, G.P.; CHIRKOV, N.M.

Kinetics and mechanism of the initial stage of polycondensation
of terephthalyl chloride with ethylene glycol. Part 2: Tempera-
ture dependence of the reaction rate.   Vysokor.
soed. 3 no.8:1170-1175 Ag '61.   (MIRA 14:9)

1. Institut khimicheskoy fiziki AN SSSR.
          (Terephthaloyl chloride) (Ethylene glycol)

27573
S/190/61/003/009/008/016
B110/B101

15.8061   2209, 2409, 1372

AUTHORS: Firsov, A. P., Sandomirskaya, N. D., Tsvetkova, V. I., Chirkov, N. M.

TITLE: Kinetics and polymerization mechanism of α-olefins on complex catalysts. IV. Polymerization of propylene in the presence of $TiCl_3$ and $Be(C_2H_5)_2$

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 3, no. 9, 1961, 1352-1357

TEXT: It was the purpose of the present paper to enlighten the role of organometallic compounds of stereospecific complex catalysts. The polymerization of propylene (P) in the presence of $TiCl_3$ and $Be(C_2H_5)_2$ was compared with that carried out with $TiCl_3$ and $Al(C_2H_5)_3$ by G. Natta (see below). The authors' experimental method was applied (Ref. 5: A. P. Firsov et al., Vysokomolek. soyed., 3, 1161, 1961). The α-modification of $TiCl_3$ was prepared according to G. Brauer (Ref. 6: Rukovodstvo po preparativnoy

Card 1/6

Kinetics and polymerization ...

neorganicheskoy khimii (Manual for preparative inorganic chemistry), M., 1956). The distilled $Be(C_2H_5)_2$ contained 3% ether. Spectroscopically pure n-heptane was used as a solvent. Polymerization was conducted at 30-70°C and 220-585 mm Hg pressure, at a molar ratio of $Be(C_2H_5)_2$ to $TiCl_3 \approx 3$. As the polymerization rate proportionally depended on the concentration of P, for both $Be(C_2H_5)_2$ and $Al(C_2H_5)_3$, the rate constant k was calculated as follows: $k = w / c_{C_3H_6} \cdot G_{TiCl_3}$ liter/min·g $TiCl_3$, where w = polymerization rate in mole C_3H_6/min; $c_{C_3H_6}$ = P concentration in n-heptane at test temperature in mole/liter, and G_{TiCl_3} = weighed $TiCl_3$ sample in g. At temperatures of 30-70°C, the polymerization rate initially increased and became then constant. At 70°C, the rate became constant earlier with the $Be(C_2H_5)_2$ co-catalyst than with $Al(C_2H_5)_3$. $TiCl_3$ samples with surfaces of 9.2 and 5 m^2/g $TiCl_3$ were used. For the steady region of polymerization, practically constant values (2.94 and 3.20, respectively) were obtained in Card 2/6

27573
S/190/61/003/009/008/016
B110/B101

Kinetics and polymerization ...

the case of $Be(C_2H_5)_2$ for the specific constant $k_{spec} = k/S_{TiCl_3}$; for

$Al(C_2H_5)_3$, however, these values were less constant (1.50 and 1.11, respectively). Nearly the same activation energies of $16,200 \pm 150$ cal/mole were obtained, from the temperature dependences of the polymerization rate for $TiCl_3 + Be(C_2H_5)_2$, irrespective of the $TiCl_3$ surface. The activation energy for $TiCl_3$ and $Al(C_2H_5)_3$, which had been previously determined (Ref. 5, see above) was 13,600 cal/mole. It resulted from the temperature dependence of the molecular weight which had been determined viscosimetrically (in Tetralin at 135°C) according to $[\eta] = 2.5 \cdot 10^{-5} \cdot \bar{M}_v^{1.00}$, and of the intrinsic viscosity at different concentrations, that the ratio $[\eta]/c_{C_3H_6}$ depended slightly on temperature and P concentration. In the laboratory of the authors, Yu. V. Kissin determined the crystallinity of polypropylene (PP), obtained in the presence of $TiCl_3$ and $Be(C_2H_5)_2$, by means of an ИКС-14 (IKS-14) split-beam spectrometer. The 840 cm^{-1} band was used for the calculation, the 1170 cm^{-1} band as the internal standard

Card 3/6

of width. Fractionation was carried out by treating the polymers with boiling and cold heptanes. Polymerization temperature practically exerts no influence upon the stereoisomeric PP composition. The co-catalyst $Be(C_2H_5)_2$ is more stereospecific than $Al(C_2H_5)_3$ and other organometallic compounds. The crystallinity of PP somewhat increases with temperature. The authors previously (Ref. 5, see above) obtained, for the temperature dependence of the polymerization rate, the equation:

$$w = \frac{k_p k_i}{\frac{1}{v}k_p + k_i} S_{TICl_4} c_0^*,$$
(3),

where k_p = constant of the rate of growth; k_i = constant of the initiation rate; c_0^* = total concentration of active centers per unit surface; v = polymerization coefficient. For an almost equal binding strength of the ethyl radical and the growing polymer chain in the catalytic complex, $k_p \approx k_i$. As v varied from 11,400 to 1900, $(1/v)k_p \ll k_i$, and (3) becomes

Card 4/6

Kinetics and polymerization ...

$w = k_p S_{TiCl_3} c_0^*$. As for the co-catalyst $Be(C_2H_5)_2$ an activation energy in the chain growth is assumed 2600 cal/mole higher than that of $Al(C_2H_5)_3$, the expression $(A S_{TiCl_3} c_0^*)$ for $Be(C_2H_5)_2$ is 45 times that for $Al(C_2H_5)_3$. The effective activation energy of the breaking of the polymer chains with $Be(C_2H_5)_2$ as a co-catalyst was determined to be 16.2 kcal/mole according to the temperature dependence of the viscosity of the resultant PP. In the case of $Al(C_2H_5)_3$, it is close to the activation energy of the chain growth, which is 14,000 cal/mole for coarsly disperse $TiCl_3$ samples. The experimental results show that organometallic compounds that react with $TiCl_3$ form a catalytic complex; the alkyl group does not affect the activity of the catalyst. The alkyl group is removed from that point of the active bond where the monomer molecules are incorporated. The metal atom, on the other hand, enters the catalytic complex during the whole chain growth, and its influence upon polymerization rate, molecular weight, and stereoisomerism of PP is, therefore, much greater than that of the

Card 5/6

Kinetics and polymerization ...

27573
S/190/61/003/009/008/016
B110/B101

alkyl group. There are 3 figures, 3 tables, and 9 references: 2 Soviet and 7 non-Soviet. The three most recent references to English-language publications read as follows: Ref. 1: J. K. Stille, Chem. Revs, 58, 541, 1958; Ref. 2: G. Natta, J. Polymer Sci., 34, 21, 1959; Ref. 8: W. Heinen, J. Polymer Sci., 134, 545, 1959.

ASSOCIATION: Institut khimicheskoy fiziki AN SSSR (Institute of Chemical Physics AS USSR)

SUBMITTED: November 1, 1960

Card 6/6

MESHKOVA, I.N.; BAKOVA, G.M.; TSVETKOVA, V.I.; CHIRKOV, N.M.

Kinetics and mechanism of the polymerization of α-olefins on complex catalysts. Part 5: Polymerization kinetics of ethylene on the catalyst system $TiCl_4 + Al(C_2H_5)_3$. Vysokom.soed. 3 no.10:1516-1523 0 '61.   (MIRA 14:9)

1. Institut khimicheskoy fiziki AN SSSR.
        (Ethylene) (Polymerization)

ENTELIS, S.G.; TIGER, R.P.; EPPLE, G.V.; CHIRKOV, N.M.

Kinetics of the reduction of diphenyl-m-tolylcarbinol by isopropyl
alcohol by hydride transfer in the system H_2SO_4 – H_2O. Dokl. AN SSSR
137 no.6:1420-1423 Ap '61.   (MIRA 14:4)

1. Institut khimicheskoy fiziki AN SSSR. Predstavleno akademikom
V.N.Kondrat'yevym.
                    (Methanol)   (Isopropyl alcohol)

MESHKOVA, I.N.; KUMAN'KOVA, S.A.; TSVETKOVA, V.I.; CHIRKOV, N.M.

Kinetics and mechanism of the polymerization of α-olefins on complex catalysts. Part 5: Kinetics of ethylene polymerization on $TiCl_4$ - $Al(iso-C_4H_9)_2Cl$. Vysokom.soed. 3 no.12:1816-1822 D '61.   (MIRA 15:3)

1. Institut khimicheskoy fiziki AN SSSR.
                (Ethylene) (Polymerization) (Catalysts)

TSVETKOVA, V.I.; FIRSOV, A.P.; CHIRKOV, N.M.

Possibility of determining elementary act constants in catalytic polymerization. Dokl. AN SSSR 142 no.1:149-151 Ja '62.

(MIRA 14:12)

1. Predstavleno akademikom V.N. Kondrat'yevym.
(Polymerization) (Catalysis)

FIRSOV, A.P.; KASHPOROV, B.G.; KISSIN, Yu.V.; CHIRKOV, N.M.

Stereospecific action of the complex catalyst α-TiCl$_3$ - Me(C$_2$H$_5$)n
in the polymerization of α-olefins depending on the nature of t he
metal of the organometallic compound. Vysokom.soed. 4 no.7:1124
Jl '62.   (MIRA 15:7)
            (Olefins)   (Polymerization)
                (Organometallic compounds)

S/020/62/145/001/013/018
B145/B101

AUTHORS: Kissin, Yu. V., Tolstykh, E. V., and Chirkov, N. M.

TITLE: Infrared spectra of the reaction products of $(C_5H_5)_2TiCl_2$ with aluminum alkyls

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 145, no. 1, 1962, 104 - 105

TEXT: The IR spectra of the "blue complexes" $(C_5H_5)_2TiCl_2Al(C_2H_5)_2$ (I), $(C_5H_5)_2TiCl_2Al(C_2H_5)Cl$ (II) and for comparison these of $(C_5H_5)_2TiCl_2$, $Al(C_2H_5)_3$, and the dimer of $Al(C_2H_5)_2Cl$ were taken and are here discussed. The complexes were prepared by reaction of $(C_5H_5)_2TiCl$ with $Al(C_2H_5)_3$ or $Al(C_2H_5)_2Cl$ in heptane. In the 1200 - 700 cm^{-1} region the spectra of the complexes correspond to the sum of the spectra of $(C_5H_5)_2TiCl_2$ plus the corresponding aluminum alkyl. The intensive 870 cm^{-1} band of $(C_5H_5)_2TiCl_2$ does not occur, whereas its 820 cm^{-1} band is shifted to 812 - 810 cm^{-1} and coincides with the absorption band of aluminum alkyl. The intensity

Card 1/2

Infrared spectra of the reaction ...   S/020/62/145/001/013/018
B145/B101

of this band is greater than the sum of optical densities of the bands corresponding to the components. 638 and 543 cm^{-1} bands in the spectrum of I may be attributed to the symmetric and antisymmetric stretching vibrations of the group $AL\begin{smallmatrix}/C\\\backslash C\end{smallmatrix}$. In II, the 620 cm^{-1} band was attributed to the deformation vibration of the CH_2 group bound on Al, and the 493 and 476 cm^{-1} bands may be ascribed to the $Al\begin{smallmatrix}/C\\\backslash Cl\end{smallmatrix}$ group. There is 1 figure.

The English-language references are: D. Breslow, N. Newburg, J. Am. Chem. Soc., 81, 81 (1959); G. Natta, J. Am. Chem. Soc., 80, 755 (1958).

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR (Institute of Chemical Physics of the Academy of Sciences USSR)

PRESENTED: February 19, 1962, by V. N. Kondrat'yev, Academician

SUBMITTED: February 14, 1962

Card 2/2

AUTHORS: Firsov, A. P., Sandomirskaya, N. D., Tsvetkova, V. I.,
            Chirkov, N. M.

TITLE: Kinetics and mechanism of α-olefin polymerization on complex
            catalysts. VI. Polymerization of propylene in the presence
            of TiCl$_3$ and Be(C$_2$H$_5$)$_2$

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 4, no. 12, 1962,
            1812-1816

TEXT: In continuation of a previous paper (Vysokomolek. soyed., 3, 1352,
1961) it has been found, with regard to propylene polymerization with
TiCl$_3$ + Be(C$_2$H$_5$)$_2$, that the rate of polymerization does not depend on the
ratio of the catalyst components or on the concentration of Be(C$_2$H$_5$)$_2$,
provided that the reaction temperature is 30°C and propylene concentration
is constant. The process of chain termination was now studied more closely
by determining the dependence of the intrinsic viscosity [η] and the
polymerization coefficient ν on the test conditions. ν is defined as being

Card 1/3

Kinetics and mechanism of...

equal to $\overline{M}/42$ or $\nu = 9.5 \cdot 10^2 [\eta]$. The following data are given for the temperature dependence of $[\eta]$ and ν:

Temperature, $^\circ$C	30	60	70
$[\eta]$, dl/g	4.70	3.15	1.90
ν	4460	2990	1800

It was moreover found that $1/\nu$ is a linear function of $1/c_{C_3H_6}$. The following data were found for the dependence of $[\eta]$ and ν on $c_{Be(C_2H_5)_2}$ at 30°C:

$c_{Be(C_2H_5)_2} \cdot 10^2$ moles/liter:	1.33	3.46	17.3
$[\eta]$, dl/g	7.9	7.00	4.5
ν	7500	6650	4270

The evaluation of these data gives an activation energy for the termination by the monomer C_3H_6 of 26.4 kcal/mole, i.e. 10.2 kcal/mole more than the activation energy for the chain growth. The activation energy for the

Card 2/3

Kinetics and mechanism of...

S/190/62/004/012/007/015
B101/B186

termination by $Be(C_2H_5)_2$ is 16 kcal/mole. The ratio $k_{term}^{Be}/k_{term}^{M}$ is 10 at 30°C, but decreases with increasing temperature owing to the higher activation energy for the termination by the monomer. There are 3 figures and 1 table.

ASSOCIATION: Institut khimicheskoy fiziki AN SSSR (Institute of Chemical Physics AS USSR)

SUBMITTED: July 3, 1961

Card 3/3

FIRSOV, A.P.; SANDOMIRSKAYA, N.D.; TSVETKOVA, V.I.; CHIRKOV, N.M.

Kinetics and mechanism of α-olefin polymerization on complex catalysts. Part 6: Polymerization of propylene in the presence of $TiCl_3$ and $Be(C_2H_5)_2$. Vysokom. soed. 4 no.12:1812-1816 D '62.   (MIRA 15:12)

1. Institut khimicheskoy fiziki AN SSSR.
        (Propene)   (Polymerization)   (Catalysts)

AUTHORS: Berdnikova, M. P., Kissin, Yu. V., Chirkov, N. M.

TITLE: Polymerization of α-amylene on complex catalysts

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 5, no. 1, 1963, 63-67

TEXT: The polymerization of 3-methyl-butene-1 and of n-pentene-1, both dissolved in n-heptane, with an $Al(C_2H_5)_3$ + $TiCl_3$ catalyst is reported. 3-methyl-butene-1 was polymerized at 40 - 70°C with a ratio of $Al(C_2H_5)_3$: $TiCl_3$ = 1.7. The constant of the reaction rate at 70°C was $2.8 \cdot 10^{-4}$ l/min·g $TiCl_3$, its temperature dependence followed the Arrhenius equation, and the activation energy was 10 kcal/mole. The polymer, a white powder, m. p. 230 - 240°C, oxidized intensively above 200°C, was insoluble in organic solvents, and did not form films. The bands identified in its IR spectrum were the following: the 1460 cm^{-1} band as asymmetric vibration of CH_3 groups and deformation vibration of CH_2 groups; a 1385 - 1366 cm^{-1} doublet as symmetrical vibrations of CH_3 in the isopropyl

Card 1/3

group. 1300 - 850 cm^{-1} bands were not identified; they disappeared almost completely in the IR spectrum of the polymer melted at 260°C. They are perhaps caused by crystal interactions in the highly crystalline solid polymer. n-pentene-1 was polymerized at 70°C. The constant of the reaction rate was $2.3 \cdot 10^{-3}$ l/min·g $TiCl_3$. The polymer is a white, rubber-like and film-forming mass, m. p. 80°C; the shape of its deformation - stress curve is typical of elastomers. The following bands were identified in the IR spectrum: 1450 and 1370 cm^{-1} bands as deformation vibrations of CH_3 and CH_2 groups, the 1340 cm^{-1} band as deformation vibration of CH groups, the 1137 cm^{-1} band as skeleton vibrations in branched polymer chains, the 1030 cm^{-1} band as pendulum swings of CH_3 groups in the polymer side chains, the 1295 cm^{-1} band as torsional vibrations of CH_2 groups, and the 727 cm^{-1} band as pendulum swings of CH_2 groups. The 1640 cm^{-1} band indicates the existence of double bonds in the end groups and the 958 cm^{-1} band the existence of trans-double bonds. The formation of these

Card 2/3

Polymerization of α-amylene on ...   S/190/63/005/001/009/020
B101/B186

bands is explained by head-on-head addition besides head-on-tail addition of the monomer and termination in the resulting compound
$\geq Al-CH-(CH_2)_2-CH-R$ caused by steric hindrance owing to the removal of
$\quad\quad C_3H_7 \quad\quad C_3H_7$

one H atom from one methylene group of the principal or side chains. There are 4 figures.

ASSOCIATION: Institut khimicheskoy fiziki AN SSSR (Institute of Chemical Physics AS USSR)

SUBMITTED: July 17, 1961

Card 3/3

ACCESSION NR: AP3000121   S/0062/63/000/005/0808/0815

AUTHOR: Meshkova, I. N.; Tsvetkova, V. I.; Chirkov, N. M.

TITLE: The chain-breaking reaction in polymerization of ethylene with TiCl sub 4 and AlR sub 2 Cl

SOURCE: AN SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 5, 1963, 808-815

TOPIC TAGS: polymerization, ethylene, kinetics, TiCP sub 4 — AlR sub 2 Cl

ABSTRACT: "The article is published in accordance with the decision of the Conference of Chief Editors of the journals of the Academy of Sciences SSSR held in 1962, as the dissertation article of N. N. Meshkova." The authors studied the kinetics of ethylene polymerization and relationships between the molecular weight of the polymer and concentrations of monomer and catalysts. Polymerization was carried out at 30C with molar ratios of AlR sub 2 Cl: TiCl sub 4 - 0.6:1-1.6:1 and ethylene pressures of 50-400 mm Hg. Forty-three milliliters of n-heptane was used as the solvent. The molecular weight of the polymer was calculated from measurements of its viscosity in tetrahydronaphthalene at 130C. It is concluded that under steady-state conditions the molecular weight of polyethylene does not depend upon the polymerization time. When the ethylene concentration is of the

Card 1/2

ACCESSION NR: AP3000121

order of 10 sup -2 M/1, the length of the chain is related to the ratio of the growth constant and the monomer concentration. The rate at which the chain is broken down into its components by the catalyst is commensurate with the break-down into monomer only at lower ethylene concentrations. No appreciable spon-taneous break-down of the chain occurred. With an increase in the molar ratios of the catalyst components, there was a sharp increase in the molecular weight of polyethylene. This was due to changes in the kinetic properties of the catalyst complex and not to a decrease in the rate of chain breaking caused by TiCl sub 4 as has been hypothesized by others. Orig. art. has: 3 tables, 8 figures.

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR (Institute of Chemical Physics, Academy of Sciences SSSR)

SUBMITTED: 28Sep62   DATE ACQ: 12Jun63   ENCL: 00

SUB CODE: CH   NO REF SOV: 006   OTHER: 005

Card 2/2

L 13543-63   EWP(j)/EPF(c)/EWT(m)/BDS   ASD   Pc-4/Pr-4   RM/WW

AUTHOR: Pirogov, O. N.; Kissin, Yu. V.; Chirkov, N. M.

TITLE: Synthesis and formation kinetics of low molecular poly-alpha-olefins on complex organometallic catalysts. 1. Polymerization of propylene in the presence of the catalytic system TiCl sub 4 and Al(iso-C sub 4 H sub 9)

SOURCE: Vy*sokomolekulyarny*ye soyedineniya, v. 5, no. 5, 1963, 633-638

TOPIC TAGS: synthesis, formation kinetics, poly-alpha-olefins, polymerization of propylene, catalytic systems

ABSTRACT: The present work was carried out to supply missing information on the polymerization kinetics of propylene over the systems Al(iso-C sub 4 H sub 9) sub 2 Cl and TiCl sub 4. Polymerization was conducted in high pressure installations at 34.8 to 17 atm and a temperature range of 60 to 100C, using liquid propane-propylene mixtures. Liquid polymers were obtained with a degree of polymerization ranging from 3 to 7 and higher. Their molecular weights depended on the temperature of polymerization and the Al:Ti ratio. Spectroscopic examination proved the polymers to be 100% olefins, with an approximate 5:1 ratio of the groups CH sub 2 = C (R) sub 2 and RHC = C(R) sub 2. A small amount of vinyl double bonds was also detected. The mechanism of double bond formation is discussed. Orig. art. has:

Card 1/2   Association: Inst. of Chemical Physics, Academy of Sciences, SSSR

KISSIN, Yu.V.; BELOYE, G.P.; YEREMINA, I.V.; VELICHEIKOVA, Ye.A.; TSVETKOVA, V.I.; CHIRKOV, N.M.

Spectroscopic criterion of the isotacticity of polypropylene. Vyskom.soed. 5 no.7:1117 Jl '63. (MIRA 16:9)
(Propylene—Spectra)

L 12584-63   EWP(j)/EPF(c)/EWT(m)/BDS   ASD   Pr-4/Pc-4   RM/WW
ACCESSION NR: AP3003301   S/0191/63/000/007/0009/0013

AUTHORS: Meshkova, I. N.; Belov, G. P.; Tsvetkova, V. I.; Chirkov, N. M. $\ell\ell$

TITLE: Polymerization of ethylene under stationary effect of heterogeneous complex catalysts

TOPIC TAGS: ethylene, TiClsub4, AlEtsub3, propane, heptane

ABSTRACT: The kinetics of polymerization of ethylene was studied in the presence of $TiCl_4$-AliBu$_2$Cl and $TiCl_4$-AlEt$_2$Cl in propane with a monomer pressure of 4 to 5 atm., and in heptane at 150mm Gh. The catalysts were tested at various concentrations with molar ratios of Al : Ti starting from 0.65 to 3 : 1 at temperature interval between 30 to 50C. The character of polymerization of ethylene in the propane media is the same as in other saturated hydrocarbons such as n-heptane. It was found that the conditions which form a stable catalytic system $TiCl_4$-Ali-Bu$_2$Cl and $TiCl_4$-AlEt$_2$Cl are obtained with low concentrations of catalyst components. These stable concentrations are with molar ratios of Al to Ti of 1 : 1 or even lower. A possibility of obtaining high stationary speeds in the process is also shown. This unables to obtain the needed quantity of polymeric
Card 1/2

L 12584-63
ACCESSION NR: AP3003301

product in a period of 2 to 4 hrs. using 0.4 to 0.7% of the total catalyst.
The polyethylene obtained at stationary conditions with the $TiCl_4$-$AliBu_2Cl$ system
in propane, has a characteristic viscosity of 3.5 to 4.2 in $100cm^3/g$, with the
rupture stress of 320 to 330 Ig force/cm^2 and relative elongation of 500-900%.
Orig. art. has: 3 tables and 4 figures.

ASSOCIATION: none

SUBMITTED: 00   DATE ACQ: 30Jul63   ENCL: 00

SUB CODE: ML   NO REF SOV: 004   OTHER: 000

Cord   2/2

KUDRYAVTSEVA, T.A.; CHIRKOV, N.M.; KOCHETKOV, N.K.

Kinetics of the substitution reaction of chlorine atoms in some aryl-β-chlorovinyl ketones. Dokl. AN SSSR 148 no.2:347-349 Ja '63.
(MIRA 16:2)

1. Institut khimicheskoy fiziki AN SSSR. Predstavleno akademikom V.N. Kondrat'yevym.
(Ketone)   (Chlorine)   (Substitution (Chemistry))